Novel Nanocomposites of Zinc-Iron Oxide: Synthesis and Characterization

A Synopsis Submitted to the

IEC University

For the award of the degree

of

Doctor of Philosophy in Physics

by

Shalini Sharma

Registration no:H15IECPHD01

Under the Supervision of

Dr. Pooja Dhiman

Department of Physics

IEC University, Baddi, (HP), INDIA

Session: 2015-16

1. INTRODUCTION: 'NANOCOMPOSITE' as the name suggests consist of two words nano and composite. Nano means of the dimension of nanoscale that means 10^{-9}m and the word composite means combination of two or more different materials which are combined to form a totally new material having wider application range as of their counterparts i.e. single material [1]. Nanocomposites can be one dimensional, two dimensional or three dimensional as dimensionality serves as key factor in determining properties of materials. The properties of nanocomposites depend on the individual components and also on the interfacial characteristics. Nanocomposites are gaining much popularity due to their properties which are of much use. We focus on nano-composites and the applications of these nanocomposites. The nanocomposites are much different from the simple composites as they have higher surface to volume ratio as compared to the simple composites. This unique property of these materials makes them much useful for use. The properties of the materials basically depend on the dimensions of the material. The dimensions play an important role in finding the properties of the given material [2]. In nanocomposite, nanoparticles such as clay, metal, carbon nanotubes act as fillers in a matrix, usually polymer matrix but not limited to it. The general class of nanocomposite organic/inorganic materials is an emerging area of research. Significant research is focused on the ability to control of the nanoscale structures via a number of synthesis techniques. The properties of nanocomposites include the unique electrical, magnetic, mechanical properties and photo catalytic and gas sensing applications etc. These materials possess high heat resistance, strength and stiffness. Many nanocomposites have been studied extensively which includes Fe_2O_3/PANI [3-7], Fe_2O_3/Graphene[8], Fe_2O_3/SiO_2[9],Fe_2O_3/ceramic composites[10][11], Fe_2O_3/Al_2O_3[12], Fe_2O_3/TiO_2[13], Fe_2O_3/ZnO. In case of polyaniline the properties of PANI are enhanced by adding

Fe_2O_3 in it. Its composites are more stable than PANI. In case of Fe_2O_3 /C we can observe the increased surface to volume ratio by adding carbon to Fe_2O_3 [14]. By combining Fe_2O_3 with another nano-composite, a new composite can be synthesized with unique and optimized properties. Composites like ZnO/CuO, ZnO/NiO [15-19] etc. are widely studied materials which have been found promising candidates for various applications. We can also see that TiO_2 is a very good photo catalyst so by combining it with Fe_2O_3 we can increase the photo catalytic activity of the material [20]. After analyzing different composites of Fe_2O_3 and ZnO, we have arrived at a conclusion that both these promising candidates can be combined to form new potential material showing remarkable properties and diverse applications.

2. LITERATURE REVIEW

A number of ZnO based nanocomposites has emerged out as promising candidates for various applications. ZnO is a good photoluminescent material which can be used as color filter in panel displays in solar cells. They have band gap of 3.4eV.ZnO is a non toxic material while other materials like CdS and GaAs are toxic. ZnO being a good potential material for photoluminescence but is degraded by U-V radiation. To avoid its degradation another material SiO_2 is added which is chemically stable and has low refractive index. The photocatalytic property of ZnO was studied and it was found that by adding Fe_2O_3 the photocatalytic activity was enhanced when it was observed under UV-visible light [21]. The ethanol sensors are getting much attention as they find application in detection of the drunken driving cases in our country which are increasing day by day. The ethanol sensing performance of α- Fe_2O_3/ZnO is much higher than pure ZnO. We can see the increasing sensitivity in this case. It has been noticed that sensitivity to detect ethanol increases by combining both the oxides and can be of great use [22]. In hydrothermal synthesis of ternary α- Fe_2O_3-ZnO-Au

nanocomposites with high gas sensing performance it was seen that ternary α- Fe_2O_3-ZnO-Au shows increased sensitivity towards butanol and acetone as compared to single α- Fe_2O_3 [23]. The photocatalytic characteristics were enhanced in case of Fe_2O_3/ZnO instead of ZnO. The photocatalytic activity of ZnO is very good but its further enhanced by adding Fe_2O_3 in it. ZnO is a good photo catalytic material and Fe_2O_3 is also a good photo catalytic material and has narrow band gap .By combining these two materials we can get a highly photo catalytic material due to its large surface area and more light absorbing ability [24]. In these years we can see that ZnO has gained attention due to its properties like wide band gap (3.37 eV) and high binding energy (60meV)[25]. Nano-composites made of Zn-Ti-Fe oxide were prepared to use as semiconductors for dye sensitized solar cells. By using these composites in the solar cells the efficiency of the solar cells was seen to increase manifold. So these oxide nano-composites play an important role in increasing the efficiency of even the solar cells [26]. The metal oxide composites have gained much importance due to high surface to volume ratio, high conductivity, and good electrocatalytic capacity for applications in electrochemical sensing technology [27]. So on the contrary the properties of nano-composites are tend to increase manifold and these properties makes the material much better to use.

3. JUSTIFICATION OF THE RESEARCH TOPIC

This topic has been chosen by taking inspiration from recent studies which shows the promising results for ZnO based nanocomposites. The properties of the material include modified electrical, magnetic, piezoelectric, luminescence, photoelectric, stability and biocompatibility, these properties makes this material highly useful. Most important application part of theses nano composites lies in photocatalysis and

sensing applications. In a race of designing a future material, we have opted ZnO: Fe_2O_3 nanocomposite for study and exploration.

4. OBJECTIVES OF THE PRESENT WORK

The main objective of our work is to synthesize ZnO based nanocomposites and then to characterize them. The synthesis and characterization will be done by different techniques. The nano-composites prepared through two different synthesis techniques will be further explored for various characterization techniques like XRD, SEM, TEM, Raman, UV-Visible Spectroscopy, XPS, Photo-luminescence (PL), Vibrating Sample Magnetometer (VSM) etc. Besides characterization techniques, nanocomposites will be studied for their applications like degradation of organic pollutants like dyes and and pharmaceutical pollutants also.

5. PROPOSED METHODOLOGY

Methodology involves the synthesis of nanocomposites by two different synthesis techniques which is solution combustion method and sol-gel route.

Solution Combustion Method

Solution combustion method is an efficient, inexpensive, and fastest route for the preparation of nano materials and nano composites. This method is normally applied for the synthesis of oxides. In this method generally metal nitrates are considered as oxides which are raw materials in process. Since this method is combustion based process, so this is followed by some fuel which serves the purpose of reducing agent and helps in the oxidation of metal nitrates. Ratio of oxidizers and fuel plays an important role in determining stechiometry of oxides or nano composites. Both these raw materials are dissolved in deionzed water with constant stirring and heating at

some moderate temperature in open air. Heating will lead to complete oxidation in open air which results into fine particles having homogenous particles symmetry.

Detailed description of Sol Gel method

In this method the colloidal solution which is known as sol is made and then it is gelated to form a continuous phase of liquid which is known as gel. In this method the liquid phase is changed into gel phase by poly condensation reaction. In this case the mixing of elements is done directly. The sol gel method reduces the disadvantages of co-precipitation in which inhomogeneous particles are formed. This method helps us to gel small size crystals.

Detailed description of Solution combustion method is the traditional method and effective method for the synthesis of nanoparticles. In this method first the oxidizer and the fuel are chosen by calculating the ratio of fuel and the oxidizer. Then the oxidizer is dissolved in the distilled water and mixed with the magnetic stirrer. Then the fuel is added and again it is stirred. The beaker is then placed on the electric heater. The boiling of the material starts followed by smoldering, flaming and fumes .After cooling the beaker the material is collected in a container and then it is send for calcinations.

The prepared nanocomposites are further characterized by various techniques mentioned as below:

1. **XRD** (X-Ray Diffraction): Discovery of X-rays is a revolution in knowing the crystalline structure at sub atomic level. X- Rays helped us to characterize is the crystalline materials and also to find the structure of the crystal. X-Ray diffraction is one of the best characterization technique used till date. Using this technique we can also find the size and shape of the unit cell of the crystal. In X-Ray diffraction

Bragg's law is the basis for finding the particle size of the crystal. The formula of Bragg's law is

$$2d_{hkl}\sin\theta_{hkl} = n\lambda$$

where d_{hkl} is the interplanar spacing θ is the diffraction and n is the integer.

2. **SEM** (Scanning Electron Microscope): SEM is a microscope that produces an image by using an electron beam which scans the surface of the specimen which is placed inside the vacuum chamber. In SEM instead of light, electron beam is used. It was built by Van Ardene in 1938. It is just like a television and uses the filament to produce electrons, magnets which move them and the detector which acts as a camera.

3. **TEM** (Transmission Electron Microscope): It operates on the same principle as the light microscope but here electrons are used instead of light. The electrons are made to pass through the specimen and an image is formed on fluorescent screen by transmitted or diffracted beam. It is used for determining the shape, size and structure of nano materials.

4. **VSM** (Vibrational Sample Magnetometer): It is an instrument which is used to measure the magnetic properties of the material. A sample is first magnetized in the uniform magnetic field and then it is sinusoidally vibrated by the use of piezoelectric material. This is based on the principle of Faraday's law of Electromagnetic induction. When a sample is placed between the electromagnets an e.m.f is induced that produces a net magnetic moment in the sample. This induced e.m.f is stimulated through data acquisition system software that helps in characterization of their magnetic properties.

5. **XPS** (X-Ray Photoelectron Spectroscopy): It is based on the principle of photoelectric effect given by Einstein. When the X-Rays were irradiated the sample with X- Rays an electron is ejected from the inner shells .The electrons which have sufficient kinetic energies come out and are known as photoelectrons. In this system the X- Rays are focused on the sample and the electrons are ejected out from the inner shells which are known as photoelectrons. The electrons then come via electron detector which count and measure the kinetic energies of the electrons. This energy is represented by the spectrum. The spectrum informs us about the elements and the compositions present in samples. The kinetic energy is given by the formula

$$K.E=h\nu-(E_B+\Phi)$$

where E_B is the binding energy and Φ is the work function.

6. **FTIR** (Fourier Transform Infra Red Spectroscopy): FTIR is a method which is used to measure the infra red spectroscopy. In infra red spectroscopy when infra red light passes through the sample, some of the radiation is absorbed and some is transmitted. The spectrum which is produced as a result shows a clear picture of molecular absorption and transmission.

7. **Raman Spectroscopy:** When a monochromatic light falls on the sample it interacts with the sample in many ways. The light is either absorbed or reflected or scattered. Raman spectroscopy is based on scattering of light. It is the scattering which tells us about the molecular structure of the material. Raman spectroscopy consist of a light source mainly coherent like lasers, sample illuminating system which consists of solid samples, liquid samples or gas samples and Raman spectrometers. When a sample is irradiated by lasers the light is either elastically or in elastically scattered. The elastically scattered radiation is known as Rayleigh scatterer and in elastically

scattered is known as Raman scatterer. The Raman scattered is further consists of stokes and anti stokes lines. Therefore in Raman scattering there is Rayleigh scattering, Stokes scattering and anti stokes scattering.

8. **UV-Visible Spectroscopy:** The principle of UV-Visible lies in the interaction of UV and visible light with matter. The range of UV falls between 200 nm -400 nm and the range of visible region lies between 400 nm -800 nm. UV and visible rays causes the transition of electron from filled energy level to higher unfilled energy level.

UV Visible Spectrometers sre used to measure the absorbbing capacity of UV or visible light by the sample.As we know the rane of UV and visible light varies fom 20nm to 800 nm.the diagram of spectrometer is shown in the figure.the light source provides visible and uv radiation ranging from 200 nm -800 nm.the light passes through the monochromator or the filter to provide light of single wavelength.it themn passes through the shutter which managaes the light.after this the light passes through either the reference cell or the smple cells and the intensities in each case is measured.let the intensity passing through the reference cell be I_0 and the intensity of light passing through the sample cell be I. Both the intensities are then measures and if Iis less than I_0 this means that the sample has absorbed some light.The absorbance is realtead to the intensities according the following relation

$$\mathbf{A=\log_{10} I/I_0}$$

9. Photocatalytic Activity: The photocatalytic removal of coloured organic compounds as toxic dyes by semiconductor metal oxides is based on advanced oxidation process (AOP). This process involves generation of radicals and reactive oxygen species on absorption of light. Advanced Oxidation Processes (AOPs) have been widely used as a reliable process for wastewater treatment since they have large

capacity to oxidise nearly all organic pollutants. Among solar AOPs, heterogeneous and homogeneous photocatalysis are the processes which have received most research attention in recent decades for wastewater treatment purposes. In the typical experimental method heterogeneous photocatalysis is generally preferred process.

6. THESIS OUTLINE

Chapter 1: Introduction

Chapter 1 **"Introduction"** includes basic introduction, history, nature, properties and various applications of nanocomposites.

Chapter 2: Literature Review

Chapter 2 **"Literature Review"** describes development and literature of concerned previous results on the ZnO based nanocomposites.

Chapter 3: Experimental techniques

Chapter 3 **"Experimental Techniques"** gives a brief description of synthesis techniques as well as the instrumentation of the experimental techniques which have been used in the present work.

Chapter 4: Results and Discussion

Chapter 4 **"Results and discussion"** presents describes the studied experimental results of structural, micro- structural, optical, and magnetic properties of prepared nanocomposites. The degradation of dyes and electrochemical sensing will be part of chapter.

Chapter 5: Summary and Conclusion

Chapter 5 **"Summary and Conclusion"** summarizes our research work in brief and presents the major conclusions drawn from the research work.

Chapter 6: Scope of Future Work

Chapter 6 **"Scope of Future Work"** includes the major suggestions for the future scope of work in this area of research.

Chapter 7: References.

REFERENCES:

[1] J. Bin Shi, C. Wei Lee, J. Wei Guo, M. Jung Cheng, C. Chieh Chang, Mater.Lett.61 (2007)5268.

[2] A. José Rodriguez, M. Fernández-García, *Synthesis, Properties, and Applications of Oxide Nanomaterials,* (John Wiley & Sons, Inc.USA, 2007)

[3] M. Blaszkiewicz,D. S. McLachlan and R. Newnham, POLYM ENG SCI, **32**

(1992) 421.

[4]. K. Anuar, S. Murali, A. Fariz and H. N. M Ekramul Mahmud, Mater.Sci.Eng.C , **10** (2004) 255.

[5]. A. Kassim, Z. B. Basar, H. N. M. Ekramul Mahmud, J.Chem.Sci,**114** (2002) 155.

[6]. S. L. Patil, S. G. Pawar, M. A. Chougule, B. T. Raut, P. R. Godse, S. Sen and V. B. Patil ,Int.J.Polym.Mater**, 61**(2012) 809.

[7]. H. Kaeami, M. F. Mousavi and M. Shamsipur, Power Sources ,**117**(2003) 255.

[8] Y. Zou, J. Kan, Y.Wang,J.Phys.Chem.C,**115**(2011)20747-20753.

[9] V. M. Bogatyrev, V. M. Gunko, M. V. Galaburda, M. V Borysenko, V. A. Pokrovskiy, E.V. Polshin, O. M. Korduban, R. Leboda,J. Skubiszewska, J. Colloid. Interface. Sci, **338** (2009)376-388.

[10] M. Evangelos: Nature Mater.**6** (2007),9.

[11] W.C. Conner, J.L. Falconer: Chem. Rev. **95** (1995),759.

[12] J. Zhang, Q. Guo, Y. Liu, Y.Cheng,Ind.Eng. Chem. Res .**51**(2012)12773-12781.

[13] M. A.Lazar,S.Varghese, S.S.Nair, .Catalysts.**2** (2012**),** 572–601.

[14] J.L. Dormann, D. Fiorani, *Magnetic properties of Fine Particles*, (North-Holland Elsevier Science Publishers, Amsterdam, 1992).

[15] Y.F.Cui, C.Wang.S.J.Wu, Chin.Phys.Lett.29 (2012)037201.

[16] F.Guo, Y. Ye, Z. X. Yang, Appl.Surf.Sci. **270** (2013)621.

[17] S. Ararwala, Z.H, Lim, E.Nicholson, Nanoscale.1(2012)194.

[18]K. Sivula, R. Zboril, F. Formal, R. Robert, A.Weidenkaff, J. Tucek, J. Frydrych, M.Gratzel, J. Am. Chem. Soc. **136**(2010)7436.

[19] J. Li, F. Meng, S. Suri, W. Ding, F. Huang, N. Q. Wu, Chem.Commmun.48 (2012)8213-8215.

[20] J. Xie, Z. Zhou, Y. Lian, Y. Hao, P. Li, Y. Wei, Ceramics International. **41**(2015)2622-2625.

[21]N. Hagura, T. Takeuchi, S. Takayama, F. Iskandar, K. Okuyama, J. Lumin. **131**(2011)138-146.

[22] D. Zhu, Y. Fu, W. Zang, Y. Zhao, L. Xing, X. Xue, Mater. Lett. **106** (2016)288-291.

[23] Y. V. Kaneti , J. Moriceau, M. Liu, Y. Yuan,Q. Zakaria,X. Jiang, A. Yu ,Sensors Actuat B **209**(2015)889-897.

[24] J. Xie, Z.Zhou, Y.Lian, Y.Hao, P.Li,Y.Wei,Ceram.Int.41(2015)2622-2625.

[25] J. Rodriguez, R .J. Candal, J. Solis, W. Estrada, M.A.Blesa, Solar Safe Water, **9** (2005)135.

[26]C. Mebrahtu, A. M. Taddesse, G. Goro, T. Yohannes, Chem. Soc. Ethiop. **31**(2017)263-279.

[27]A. Hayatt, J. L. Marty, Sensors.**14** (2014)10432.

RESEARCH SCHOLAR

SHALINI SHARMA

Research Scholar,

Registration Number:

Deptt. of Physics

IEC University, Baddi (HP), India

SUPERVISOR(S)

Dr. POOJA DHIMAN

HOD,

Deptt. of Physics

IEC University, Baddi (HP), India